Experimental Identification of Design Parameters for Novel Reactor–Separator

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The separation of methanol from glycerin and biodiesel in biodiesel manufacturing significantly adds to the cost of the biodiesel. A novel reactor–separator, based on flowing effluents through a temperature gradient, keeps the methanol in the reactor and could decrease the cost of separating methanol from glycerin and biodiesel. The reactor–separator has a lateral extension at the bottom of the reactor, which is referred as the "auto-recycle discharge." This discharge replaces a conventional flash separator and condenser. The ability of the auto-recycle discharge to remove methanol from glycerin and biodiesel was experimentally evaluated at discharge temperatures ranging from 60 to 180°C and pressures from 101 to 515 kPa. Exiting compositions approached methanol's bubble point compositions under the assumption of a nonvolatile second component (either glycerin or biodiesel), and this constraint largely defined the separation that was achieved. Glycerin with less than 2% methanol was obtained using this separator. When extended for the separation of methanol from biodiesel, less than 1% methanol remained in the biodiesel effluent. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 1207–1213, 2005

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Introduction

Expansion of the world's biodiesel industry is significantly limited by high capital costs of the biodiesel refineries. The process of biodiesel production is referred to as *alcoholysis* (a type of transesterification), in which methanol reacts with oils and fats to give methyl esters and glycerin. Separation of the glycerin from biodiesel is achieved by decanting the glycerin phase because the two components are substantially immiscible. Methanol is soluble in both biodiesel and glycerin, presenting the need for additional flash or distillation separation processes.

The present work evaluates the feasibility of removing methanol from both glycerin and biodiesel by flowing these products through a temperature gradient in such a manner that the methanol is flashed from the products and sent back into the reactor before discharge. Figure 1 compares the reactor–separator to a conventional configuration. The conventional configuration uses a flash column to remove methanol from glycerin and biodiesel. The reactor–separator has a lateral discharge extension that uses a temperature gradient to drive methanol out of the glycerin phase and into the reactor. The extension is referred to as *auto-recycle discharge* and replaces the flash separator and condenser, thus alleviating the need for storing crude glycerin containing >20% methanol.

As a result of this relatively simple design:

(1) A substantially methanol-free glycerin phase is discharged from the reactor.

(2) Methanol is inherently forced back into the biodiesel phase where it can be used to drive high conversions to the biodiesel product (reaction is equilibrium limited).

(3) Biodiesel is discharged substantially methanol-free and the methanol is forced back (recycled) into the reactor and any enthalpy of condensation is effectively used to heat influent reagents.

This approach can be used in either a semibatch or continuous mode. In a semibatch mode, up to 10% of the biodiesel and

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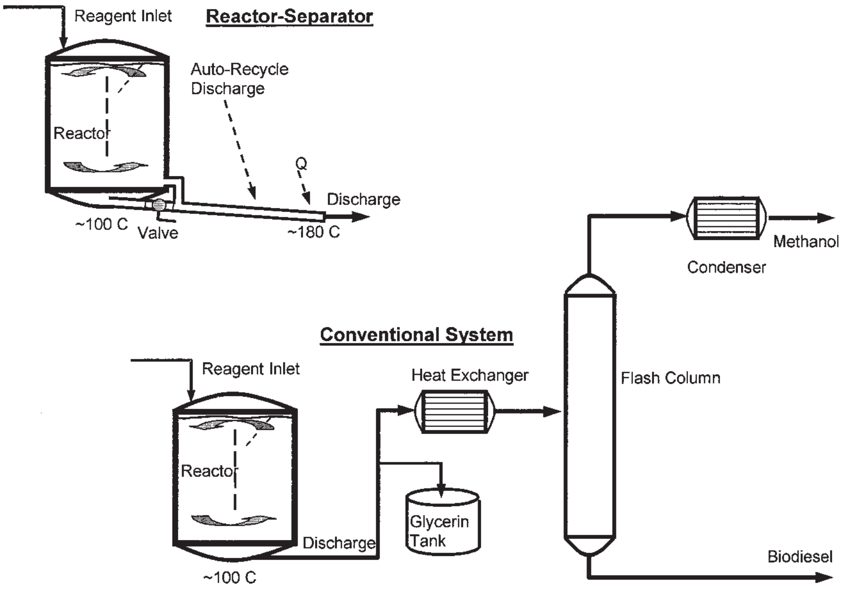

Figure 1. Conventional system and a reactor–separator that uses temperature gradients to drive out methanol from glycerin and biodiesel discharge.

glycerin may be kept in the reactor from one batch to the next with only a corresponding 10% reduction in reactor capacity. This glycerin and biodiesel help solvate the methanol. By the end of a batch, a mixture of about 50% methanol, 25% glycerin, and 25% biodiesel may be at about 120°C (being at 90°C at the start of glycerin discharge from that batch). This 120°C liquid and respective methanol vapors (under pressure) are mixed with oils/fats and methanol from the new batch and, in so mixing, the energy used for driving the methanol out of the products of the previous batches is recovered in the reagents of the new batch. The net impact is that more energy is recovered by this method than is typical with conventional batch processes.

Potential advantages of this design and mode of operation are:

(1) Reduced energy costs associated with removing and recycling methanol

(2) Eliminated equipment costs (flash column, condenser, and storage tank)

(3) A 1.5 × stoichiometry of methanol provides essentially the same driving force for biodiesel production as a 2.5 × stoichiometry does in a conventional reactor not having the in situ recycle of methanol

(4) A smaller and simple refinery system is easily prefabricated and mobile further reducing the cost of the system and allowing for quicker delivery

(5) No water is used in the process and the crude glycerin phase (containing <2% methanol) is ready for sale or upgrading without further processing

Background

Over the past couple of decades fatty acid methyl esters derived from vegetable oil and animal fat have assumed importance as a potential diesel fuel extender known as biodiesel, with worldwide consumption approaching a billion gallons per year. The methyl esters also find value in a variety of applications including use as phase-change materials. Methyl esters of fatty acids are produced by alcoholysis of triglycerides with methanol in the presence of an acid or a base catalyst, as illustrated by reaction Scheme 1. Complete conversion of the triglyceride involves three consecutive reactions with monoglyceride and diglyceride intermediates[1]:

$$\left.\begin{aligned} \text{Triglycerides} + CH_3OH &\rightarrow \text{Diglycerides} + R_1COOCH_3 \\ \text{Diglycerides} + CH_3OH &\rightarrow \text{Monoglycerides} + R_2COOCH_3 \\ \\ \text{Monoglycerides} + CH_3OH &\rightarrow \text{Glycerin} + R_3COOCH_3 \end{aligned}\right\} \text{Biodiesel} \tag{1}$$

This reaction is equilibrium limited and, typically, a 2 × stoichiometry of methanol is used to drive the reaction to the right (to biodiesel formation). To meet ASTM biodiesel specifications, the glycerin phase is often removed, additional methanol added, and a second stage of reaction is performed to obtain yields in excess of 98%. The glycerin separation is

Table 1. Data for Semibatch Separation of Glycerin–Methanol Mixture with Horizontal Orientation of the "Auto-Recycle Discharge" with Different Residence Times

T_1 (°C)	Residence Time (min)	Xp (wt %)	Xc (wt %)	P_2 (kPa)	Xf (wt %)	T_2 (°C)	SD in Xp
200	18	1.29	57.35	186	20	82	0.12
200	11.5	1.65	56.98	186	20	82	0.08
180	21.5	1.24	64.17	158.5	20	82	0.25
180	10.5	2.6	65.5	117.2	20	75	0.16
180	7.5	2.87	51.25	117.2	20	75	0.07
140	21.5	3.3	56.17	103.4	20	75	0.07
140	10.5	5.46	55.57	103.4	20	75	0.14
140	7.5	5.57	54.97	89.6	20	75	0.08
110	21.5	8.16	54.48	89.6	20	75	0.11
110	10.5	8.19	54.47	89.6	20	75	0.2
110	7.5	8.56	54.48	89.6	20	75	0.11
110	40	19.12	20.42	413.5	20	25	0.1
75	21.5	18.91	21.37	0	20	25	0.02
75	10.5	18.74	21.37	0	20	25	0.02
75	7.5	18.74	21.37	0	20	25	
75	40	18.45	21.3	413.5	20	25	0.31
60	60	18.93	20.75	0	20	25	0.52

facilitated by the formation, at high conversions, of a heavy glycerin phase that can be decanted from the light biodiesel phase. In the decanting much of the methanol is removed in the glycerin phase because the methanol preferentially distributes into the glycerin phase (about 40% in glycerin with 5% methanol in the biodiesel). Figure 1 illustrates the process concept. The most important feature of this system is the temperature gradient that exists between the 180°C glycerin discharge and the reactor at temperatures between 60 and 100°C. Methanol is driven from the discharge where it has a high activity (flashing at the pressure of operation) to the reactor where it is soluble in the "cooler" methyl ester phase.

Thermal diffusion

One of the mechanisms for separation in the presence of temperature gradients is *thermal diffusion*. The primary difference between much of the work reported in this study and thermal diffusion separation is that the pressures in the reactor–separator of this study are sufficiently low to allow flashing to occur at the hotter temperatures at the discharge end of the auto-recycle discharge extension.

The use of irreversible processes involving nonisothermal solution behavior for separating liquids has been reported in the past several decades. Nonisothermal solution behavior has two manifestations, one the inverse of other. If two gases of different compositions and initially at the same temperature are allowed to diffuse together, a transient temperature gradient results from the ordinary diffusion process. This phenomenon was first noted by Dufour[2] in 1873, and bears his name. Conversely, if a temperature gradient is applied to a homogeneous solution, a concentration gradient is usually established. The designation "thermal diffusion " is generally applied to this second effect.[3] The existence of thermal diffusion in the liquid state has been known for nearly 100 years. In 1856 Ludwig[4] observed that when an aqueous solution of sodium sulfate was subjected to a temperature gradient a concentration gradient was established. Soret[5] discovered the same effect using solutions of potassium nitrate and sodium chloride. This phenom-

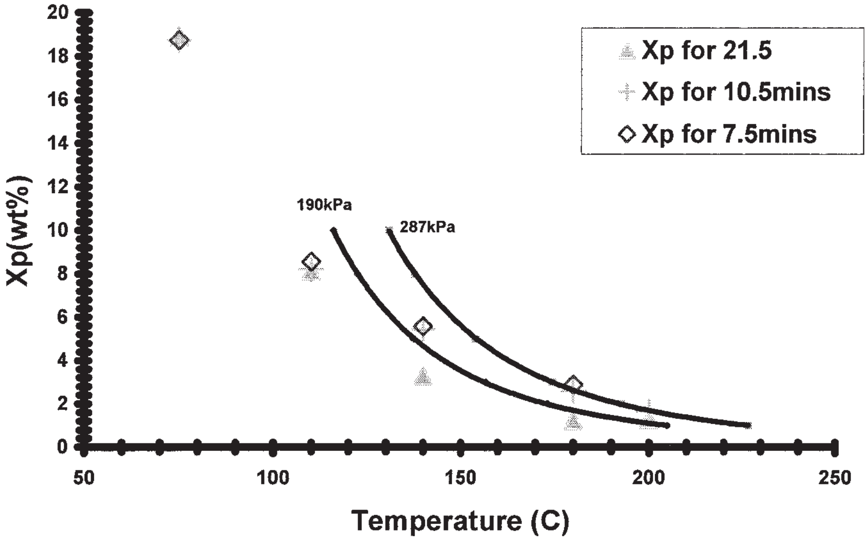

Figure 2. Graph showing effect of temperature on *Xp* for different residence time for glycerin–methanol system.

Table 2. Data for Semibatch Separation of Biodiesel–Methanol Mixture with Horizontal Orientation of the "Auto-Recycle Discharge"

T_1 (°C)	Residence Time (min)	Xp (wt %)	Xc (wt %)	P_2 (kPa)	Xf (wt %)	T_2 (°C)	SD in Xp
180	~10	0.63	28.01	138	10	75	0.04
140	~10	1.21	17.74	138	10	57	0.15
110	~10	2.34	12.56	138	10	42	0.42
75	~30	7.22	11.64	138	10	30	0.49
75	~10	7.31	11.43	413.5	10	30	0.21
60	~60	10.19	10.21	138	10	25	0.39

enon is referred to as the Ludwig–Soret effect, or more frequently the Soret effect.[6]

Several researchers have separated mixtures of different isotopes and several binary organic mixtures using this effect.[7-9] Parallel-plate or concentric-cylinder types of apparatus are exclusively used in separating the liquids by thermal diffusion. Prigogine and coworkers[10-12] investigated the Soret coefficient of various solutions using the thermogravitational method of separation in a parallel-plate–type apparatus. Jones and associates[13,14] separated various complex petroleum oils into fractions or varying viscosity index using concentric-cylinder–type apparatus. In the present study the apparatus used is the novel reactor–separator that is different from the normal thermal diffusion apparatus. In the current study, pressure was varied to go from a regime where thermal diffusion controls separation to a regime where flashing with respective convective separation occurs.

Experimental Setup and Procedure

The apparatus used to conduct experiments included a laboratory-scale 1-L cylindrical vessel capable of operation to 1800 psig. A stainless steel tube (ID, 1/2-in.; length, 13 in.) was connected laterally to this vessel. The tube was connected in such a way that it remains tilted downward by 1 in. The slope helps the methanol vapors to move upward and back into the vessel. A 500-W heating cable was used to supply heat by wrapping the cable tightly around 4 in. at the discharge end of the tube. Cooling water coils were wrapped around the vessel to control the temperature of the vessel when the discharge end was heated to higher temperatures. The hot discharge end was connected through a globe valve first to an air-cooled coil that was connected to the metering pump. The temperatures were measured and controlled by a Camile 2000 data acquisition and control system and with Camile TG 4.1 software.

At the start of an experiment from 400 to 600 mL of 20% methanol in glycerin (or 10% methanol in biodiesel) was charged to the tank. The vessel and auto-recycle discharge were heated to targeted temperatures and then a constant overpressure of nitrogen was applied to maintain vessel/tube pressures. When the discharge end reached the set-point temperature, the pump was started that metered liquid from the discharge tube. Care was taken so that hot effluent from the auto-recycle discharge was cooled sufficiently to prevent any loss of methanol vapors from the pump outlet.

Effluent samples were collected at the discharge of the metering pump. Samples were taken every 0.5 h after reaching steady state. Samples of effluent were collected until steady state was obtained, as demonstrated by three consecutive discharge samples having the same composition.

Method of Analysis

Samples were analyzed using a Hewlett–Packard 6890 GC (Wilmington, DE) equipped with a split–splitless injection system. Data collection and analysis were accomplished with Hewlett–Packard Chemstation software. A Restek Corp. (Bellefonte, PA) MXT®WAX 70624 GC column (30 m × 250 μm × 0.5 μm) was used for separation with a Hewlett–Packard 5973 mass selective detector and flame ionization detector. Samples were dissolved in dimethyl sulfoxide (DMSO) and 1-propanol was added as an internal standard.

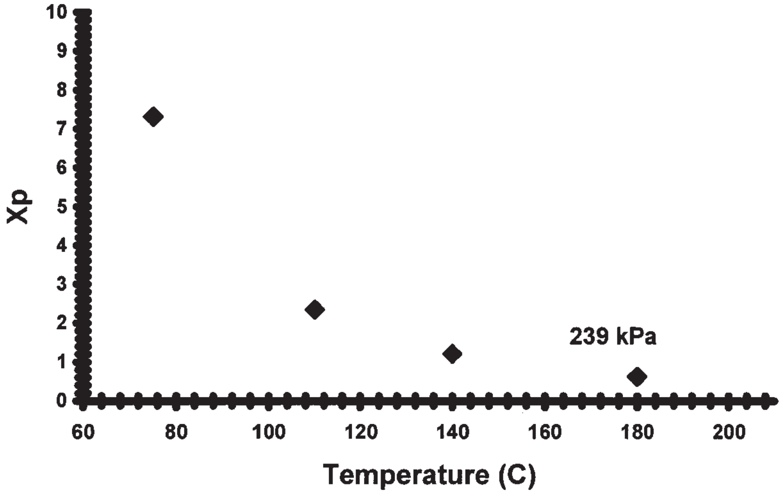

Figure 3. Graph showing effect of temperature on *Xp* at 20 psi pressure for biodiesel–methanol system.

Table 3. Data for Semibatch Separation of Glycerin–Methanol Mixture with Vertical Orientation of the "Auto-Recycle Discharge"

T_1 (°C)	Residence Time (min)	Xp (wt %)	Xc (wt %)	P_2 (kPa)	Xf (wt %)	T_2 (°C)	SD in Xp
180	~60	1.45	62.54	158.5	20.0	82	0.35
160	~60	4.27	42.09	127.5	20.0	75	0.45
140	~60	7.35	35.29	103.4	20.0	75	0.13

About 2 μl of the sample was injected into the column. The oven temperature program includes starting at 40°C (2 min), ramping at 15°C/min to 230°C and holding for 2 min at 230°C. Elution times are methanol, 1.15 min; glycerin, 14.7 min; 1-propanol, 2.29 min. Standard calibration curves allowed the peak areas of the components, divided by the peak area for 1-propanol, to be directly converted into concentration. A refractrometer was also used to detect methanol in the samples. The results from GC analysis and refractrometer measurements were compared and both were similar, except GC results were more accurate.

Results and Discussion

A series of experiments were conducted to evaluate the following parameters that can impact the performance of separation:

- Temperature of the discharge end of the tube over which the temperature gradient was applied
- Orientation of auto-recycle discharge, horizontal (with slight slope) vs. vertical
- Rate of removal of the effluents or the residence time of the mixture in the case of glycerin–methanol mixture

Batch (no flow) and semibatch (with flow from discharge) studies were conducted. Some semibatch studies were conducted at a constant static pressure created by nitrogen addition to the system.

Effect of temperature on separation for glycerin–methanol mixture and mechanism of separation

Table 1 summarizes the results of the experiments carried out at different temperatures for feed of 20% methanol in glycerin. At higher discharge end temperatures, methanol concentrations were <2%. At discharge end temperatures of 200 and 180°C the X_p (exiting methanol mass fraction) was 1.28 and 1.24%, respectively, whereas at temperatures of 140 and 110°C for the same residence time X_p values were higher at 5.46 and 8.19%, respectively. The final concentration of methanol in the vessel at the end of the experiment is between 55 and 65%. The pressures indicated in Table 1 result from the initial air in the system when the vessel is sealed plus the vapor pressure of methanol at the vessel temperature.

Figure 2 shows the effect of temperature of the discharge end of the auto-recycle discharge on separation for different residence times in the auto-recycle discharge tube (extension). The temperature has the greatest impact on separation with higher temperatures producing lower concentrations in the product. However, at 200°C the separation is only marginally better than that at 180°C. An optimal separation appears to be reached at a temperature difference of about 100°C between the vessel and the discharge.

At higher temperatures, the relative volatility that drives the separation diminishes. Constant pressure bubble point curves are superimposed and indicate that performance is driven by the bubble point compositions at the hot end of the auto-recycle discharge.

Residence time also has an impact, with higher residence times leading to better separations. The likely separation mechanism is the flashing of methanol from glycerin as it flows through the extension. The hot methanol vapors moves upward and back into the vessel, condensing in the cooler fluids of the vessel. This mechanism was visually confirmed in a batch experiment with a glass tube.

In these semibatch studies the concentration of methanol increased from the initial loading of 20% to up to 65%. For experiments having higher discharge temperatures, the methanol became more concentrated in the vessel and conduction of heat to the vessel was also greater, resulting in higher pressures. Further studies were conducted at a constant static pressure to remove this variable from the experimental design.

The series of experiments summarized in Table 1 included study with the hot end of the discharge tube at 75 and 60°C and a pressure of 141 kPa. This pressure is considerably higher than the bubble point pressure of the glycerin–methanol mixture and, yet, the concentration of methanol decreased from 20 to 18.45 and 18.91%, respectively. This separation is likely explained by the Soret diffusion (or thermal diffusion) arising from the temperature gradient between the discharge end and the vessel.

Effect of temperature on biodiesel–methanol system

Table 2 summarizes the results for separations of 10% mixture of methanol in biodiesel at a constant pressure of 236 kPa. For a discharge end temperature of 180°C the methanol concentration was reduced to 0.64%. Similar to glycerin–methanol mixture, higher temperatures lead to better separations and lower methanol concentrations in the discharge. Figure 3 exemplifies these trends.

Table 4. Data for Semibatch Separation of Glycerin–Methanol Mixture with Horizontal Orientation of the "Auto-Recycle Discharge"

T_1 (°C)	Residence Time (min)	Xp (wt %)	Xc (wt %)	P_2 (kPa)	Xf (wt %)	T_2 (°C)	SD in Xp
180	60	0.63	62.13	158.5	20.0	82	0.17
140	60	3.35	56.23	103.4	20.0	75	0.12
110	60	7.8	55.23	89.6	20.0	75	0.09

Table 5. Data for Semibatch Separation of Glycerin–Methanol Mixture with Horizontal Orientation of the "Auto-Recycle Discharge" with Valves

T_1 (°C)	Residence Time (h)	Xp (wt %)	Xp_1 (wt %)	Xp_2 (kPa)	Xp_3 (wt %)	Xc (°C)	SD
140	6	3.27	16.17	25.15	47.47	56.93	0.37
100	6	9.47	17.46	26.12	40.14	52.14	—

As compared to methanol–glycerin mixture for the same temperature of discharge end, the biodiesel–methanol mixture has lower methanol concentration. This is primarily attributed to the higher activity of methanol in biodiesel compared to that of methanol in glycerin. Whereas glycerin has strong hydrogen bonding with methanol, leading to low activity coefficients, biodiesel does not hydrogen bond and has a larger molecular weight—both leading to high activity coefficients.

Effect of orientation of auto-recycle discharge on separation

Tables 3 and 4 summarize the results of experiments carried out for horizontal and vertical positions of auto-recycle discharge. Results show that at 180 and 140°C the discharge methanol concentrations for vertical orientations are 1.45 and 7.35%, respectively. At similar temperatures the methanol discharge compositions for the horizontal orientation are 0.63 and 3.35%, respectively, which are almost half the value for vertical orientation. This is likely a result of convective mixing in the vertical tube arising from the expansion of the glycerin phase as it is heated. The methanol vapors will also tend to lead to greater mixing in the vertical configuration. Based on these results, the near-horizontal position of the auto-recycle discharge is the preferred configuration.

Study of concentration gradient for horizontal orientation

A more-detailed study of the concentration profile along the auto-recycle discharge was performed by dividing it into five separate sections of equal length using globe valves. The valves were kept open when the tube was heated and temperature gradient was maintained. After heating for sufficient time to achieve steady state the heating tapes were turned off. The valves were kept open for a few minutes to allow the vapors to flow from the hot end to the cold end, after which they were closed, thus trapping liquids of different concentrations in each section. The concentration profiles in these sections are summarized in Table 5. At 140°C the methanol concentration was 3.27% at the hot end and 56.93% at the cold end, with a continuous increase in methanol concentration between the ends.

Effect of flow rates for semibatch system for glycerin–methanol mixture

For semibatch processes with continuous removal of effluent from the vessel, the effluent methanol concentrations depend on the flow rate through the tube. More specifically, the residence time in the discharge tube is an important design heuristic. Table 1 summarizes the impact of different residence times, which is graphically represented by Figure 4. For a discharge end temperature of 180°C and residence times of 21.5 min, the methanol effluent concentration is 1.24%, whereas at the same temperature for residence time the 7.5-min concentration is 2.87%. The residence time appears to have a greater effect on separation at higher temperatures.

Cumulative impact

During the investigations of the reactor–separator, discharge temperatures, reactor temperature, and reactor pressure were

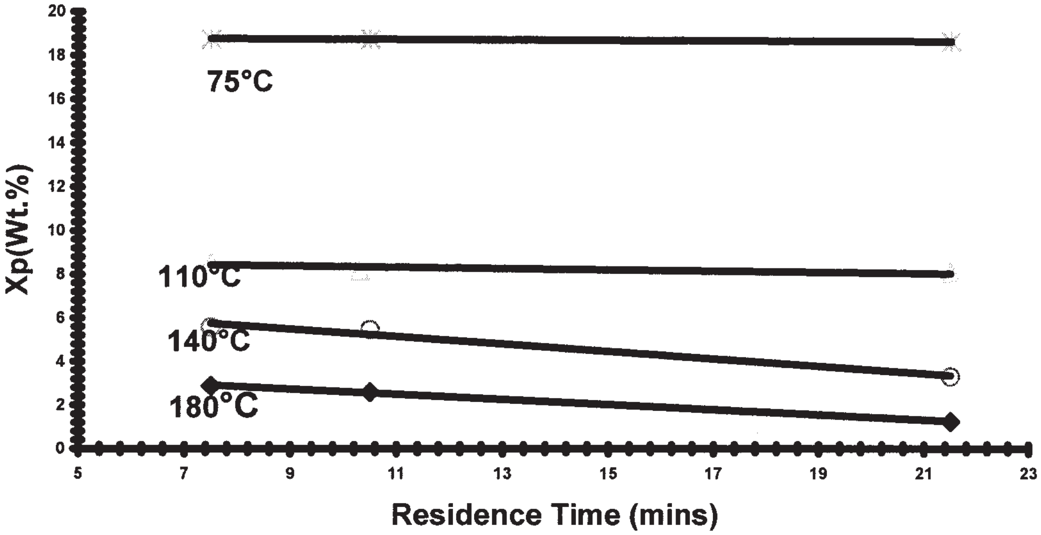

Figure 4. Graph showing concentration of methanol in glycerin as a function of residence time with temperature as a parameter.

each varied. A sufficient number of experiments were taken to decouple the effects, which is substantially summarized by Figures 1 and 2. The system pressure (essentially constant throughout) and the discharge temperature have a greater impact than the reactor temperature, as indicated by these figures, where separation approaches a bubble point composition largely determined by these two parameters. The system pressure, however, is a function of the reactor composition, temperature, and any static pressure created by inert gases in the system.

Design considerations

The most common temperature-driven reaction–separation is reactive distillation. Much has been published on reactive distillation. However, the reactor–separator is different from reactive distillation in the following ways.

(1) The reaction residence time for biodiesel in the reactor of Figure 1 is from 4 to 20 h. This residence time is far greater than that encountered in a reactive distillation system.

(2) Because of the need for high residence times, the fraction of vapor in the reaction should be kept at a minimum ($<$10% of the reactor volume), which is inconsistent with distillation in which typically $>$70% of the void reactor volume is vapor, with $<$30% being liquid.

(3) The reactor separator of this system returns the heat back into the reactor where it is recovered by the next batch. In distillation the heat leaves the system and is lost in the condenser.

Based on the fundamental interpretations provided in this section, the reactor–separator of this study could be applied to other systems where reagents have high relative volatilities compared to those of the products. A sequence of considerations is suggested when designing reactions using this reactor–separator, including:

(1) The vessel (reactor) temperatures should be optimized relatively independently of the separation temperatures, including such factors as pressure required to maintain liquid phases, materials of construction that can contain the temperatures, and product selectivity.

(2) The pressure should be maintained at the bubble point of the reaction mixture (at the reactor temperatures) because lower pressures result in higher relative volatilities for better separations in the discharge tube.

(3) The separation appears to be most effective when the highest temperature in the auto-recycle discharge is about 100°C warmer than the reactor temperature.

In practice, these heuristics would provide a base case for optimization specific to the reaction of interest.

Conclusion

A novel reactor–separator that uses temperature gradient to drive separation in effluents has been demonstrated as useful in biodiesel production. This technology has the ability to continuously remove methanol from glycerin and biodiesel effluents, removing methanol to concentrations $<$ 1 wt %.

The temperature of the auto-recycle discharge has the greatest impact on separation, with higher temperatures leading to better separation under the conditions of this study. In practice, the reaction conditions should be used to identify a reasonable reactor cost. Lower pressures promote better separations and thus the system should operate at the bubble point of the reaction mixture. Optimal temperatures of the discharge are about 100°C greater than the reactor temperature. Separations were observed to improve with increasing residence times up to about 20 min. The orientation of the auto-recycle discharge influences separation; near-horizontal orientation is preferred with the discharge end lower.

Acknowledgments

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Notation

Xp = concentration of methanol coming out of the auto-recycle discharge
Xc = concentration of methanol in the reactor after separation
Xf = concentration of methanol in feed
T_1 = temperature at the discharge end of auto-recycle discharge
T_2 = temperature of the tank

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